



**TRANSLATION**

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## Patent Application

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5 To: Mr. Hideo Saito, Governor of Japanese Patent Office

### 1. Title of the Invention

Method for the analysis of nitrogen oxide

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## **SPECIFICATION**

### 1. Title of the Invention

Method for the analysis of nitrogen oxide

### 2. Patent Claims

A method for the analysis of nitrogen oxide, characterized by using the following procedure.

First, the nitrogen oxide present in the exhaust gas is converted to nitrogen pentoxide and nitric acid with ozone and then pyrolyzed to form nitrogen dioxide. The nitrogen dioxide is determined without removing the water present in the exhaust gas through a process not affected by the water or through a process of further converting the nitrogen dioxide to nitrogen monoxide, followed by removing the water and then determining the amount of nitrogen oxide using CLA, NDIR, or electrolysis at constant potential.

### 3. Detailed Explanation of the Invention

This invention is related to a method for the quantitative analysis of nitrogen oxide ( $\text{NO}_x$ ), particularly a trace amount of  $\text{NO}_x$  present in exhaust gas.

$\text{NO}_x$  capable of causing air pollution is mainly formed by nitrogen monoxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ) and can be determined quantitatively with the following methods.

#### (1) Chemical luminescence assay (CLA)

In this method, NO is oxidized with ozone ( $\text{O}_3$ ) and the  $\text{NO}_2$  formed is determined through chemical luminescence.

#### (2) Non-diffused infrared spectroscopy (NDIR)

In this method, NO is determined directly through its absorption in the infrared region.

#### (3) Non-diffused UV spectroscopy (NDUV)

In this method,  $\text{NO}_2$  is determined directly through its absorption in the UV region.

#### (4) Electrolysis at constant potential

In this method, NO and  $\text{NO}_2$  are determined in an electrolyte solution by electrolysis.

#### (5) Correlated spectroscopy

In this method, accuracy is improved by utilizing absorption at multiple wavelengths. The method has been developed recently and is based on the same mechanism as in Methods (3) and (4).

5

When using the methods described above in the analysis of  $\text{NO}_x$  present in exhaust gas, the result will be affected by the water present in the exhaust gas. Therefore, the water must be removed to a certain degree or the analysis should be carried out on the partially dried exhaust gas.

- 10 In addition to  $\text{NO}_x$ , exhaust gas also contains water,  $\text{SO}_2$ , CO,  $\text{CO}_2$ , etc., and these components may adversely affect the analysis of  $\text{NO}_x$ . Particularly, the water present in exhaust gas is able to affect significantly the result obtained from the quantitative analysis of  $\text{NO}_x$ .

However, when the water is removed, the concentration of  $\text{NO}_x$  is also decreased.

15

The  $\text{NO}_x$  present in the exhaust gas generated from a furnace, such as boiler, etc., contains mainly NO, which is not very reactive and may not be easily lost during the process of removing water. In other words, the concentration decrease of  $\text{NO}_x$  is not a serious problem.

- 20 However, the  $\text{NO}_x$  present in the exhaust gas generated from a diesel engine or an acid-washing plant may have a high concentration and contains mainly  $\text{NO}_2$ , which is very reactive and may be easily lost during the process of removing water. In other words, the accuracy of the quantitative analysis of  $\text{NO}_x$  can be affected significantly.

- 25 Table 1 shows an example of the results obtained from the quantitative analysis of  $\text{NO}_x$ . The analysis was carried out for the exhaust gas generated from a diesel engine with PDB (phenol-disulfonic acid) method and CLA method. Significant variation can be observed from the same exhaust gas for the concentration of  $\text{NO}_x$  obtained with the two methods.

30 Table 1

Conditions	PDB method	CLA method
A	750 ppm	590 ppm
B	890 ppm	770 ppm
C	980 ppm	770 ppm

Due to the strict regulations on exhaust gas pollution, various measures have been taken regarding exhaust gas released from boilers. As a result, the concentration of  $\text{NO}_x$  in the exhaust gas is further reduced. On the other hand, however, the concentrations of species with an oxidation state higher than that of  $\text{NO}_2$ , such as nitrous acid ( $\text{HNO}_2$ ) and nitric acid ( $\text{HNO}_3$ ), may increase. For the two high-oxidation-state species, the current methods for determining the concentration of  $\text{NO}_x$  described above as well as the related pretreatment methods are not effective.

The purpose of this invention is to solve the problems mentioned above and to provide a method for the quantitative analysis of nitrogen oxide ( $\text{NO}_x$ ), particularly a trace amount of  $\text{NO}_x$  present in exhaust gas. In the method of this invention, the  $\text{NO}_x$  present in exhaust gas is first converted to  $\text{NO}_2$ . The  $\text{NO}_2$  is then determined directly or the  $\text{NO}_2$  is reduced to  $\text{NO}$ , which is then determined quantitatively.

In the method of this invention, the  $\text{NO}_x$  present in exhaust gas is first oxidized with  $\text{O}_3$  to nitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) and nitric acid ( $\text{HNO}_3$ ), which are then pyrolyzed to form  $\text{NO}_2$ . Next, the  $\text{NO}_2$  formed in the exhaust gas is determined quantitatively using a procedure for determining  $\text{NO}_2$  not affected by the water present in the exhaust gas, so that the amount of  $\text{NO}_x$  present in the exhaust gas can be determined. Also, the  $\text{NO}_2$  formed in the exhaust gas can be first reduced to  $\text{NO}$ , followed by dehydration, and then the amount of  $\text{NO}_x$  present in the exhaust gas can be determined by measuring the amount of  $\text{NO}$  with a common method, such as CLA, NDIR, or electrolysis at constant potential.

In other words, the  $\text{NO}_x$  present in exhaust gas is completely converted to  $\text{NO}_2$  before the exhaust gas is introduced into the system for quantitative determination of  $\text{NO}_x$ .

The  $\text{NO}_x$  present in exhaust gas can be quantitatively determined with the following methods through  $\text{NO}_2$  even when the exhaust gas contains water.

Since the procedure for quantitative determination of  $\text{NO}_x$  is not affected by the water present in exhaust gas, for example, the exhaust gas is first introduced into a gas-sealed cell without removing the water. Then, the concentration of  $\text{NO}_x$  is determined quantitatively using the UV absorption of  $\text{NO}_2$ . The concentration of  $\text{NO}_x$  can also be determined quantitatively using ESR.

Moreover, quantitative determination of  $\text{NO}_x$  can also be achieved by passing the  $\text{NO}_2$ -containing exhaust gas through a  $\text{NO}_2$ -converter capable of converting  $\text{NO}_2$  to  $\text{NO}$  with the CLA method, followed by dehydration and quantitative determination with the CLA method, NDIR method, or electrolysis at constant potential.

5

Since the  $\text{NO}_x$  present in exhaust gas is completely converted to  $\text{NO}_2$  before the exhaust gas is introduced into the system for quantitative determination of  $\text{NO}_x$ , the method of this invention is also suitable for the exhaust gas, which has been treated with other treatment methods recently adopted for exhaust gas. In the method of this invention, the  $\text{NO}_x$  present in exhaust gas is all converted with any loss. Therefore, a trace amount of  $\text{NO}_x$  present in exhaust gas can be determined quantitatively at a high accuracy.

10

The method of this invention can be used for the quantitative determination of  $\text{NO}_x$  present in exhaust gas generated from a combustion device, such as boiler, heating furnace, gasoline engine, diesel engine, etc., for the quantitative determination of  $\text{NO}_x$  present in exhaust gas generated from a combustion-type exhaust gas treatment plant, and for the quantitative determination of  $\text{NO}_x$  present in exhaust gas generated from an iron and steel plant, a chemical plant, etc.

15

In the following, this invention is explained in more detail with practical examples together with the figures attached.

20

Figure 1 shows the flow chart for the method of this invention. The system for the quantitative determination of  $\text{NO}_x$  consists of exhaust gas sampling part,  $\text{O}_3$  generating part, oxidation reaction part, pyrolysis part, and measurement part.

25

#### Exhaust gas sampling part

The  $\text{NO}_x$ -containing exhaust gas coming from exhaust gas source 1 is sampled through sampling probe 2, dust filter 3, pipeline 4, and pump 5. The gas sample is then sent through pipeline 6 to flow rate regulator 7 and flow meter 8. After the flow rate is adjusted, the gas sample is supplied to oxidation reaction chamber 16.

30

In order to prevent the problems caused by water condensation from the sample gas, the exhaust gas sampling part should be maintained at a temperature higher than the boiling point of water,

preferably a temperature of 110°C or higher using heating device 22, which consists of a heater and insulating material.

5 Solid substances, such as ash, etc., are removed through filter 3. Filter 3 can also be installed on the tip of sampling probe 2.

In order to control the gas flow rate, a vent is installed on pipeline 6, so that excess material can be discarded from the system. Flow meter 8 may use various structures, including orifice, etc.

10 Sampling probe 2, filter 3, pipeline 6, pipeline 9, etc., can be made of stainless steel, quartz, glass, etc.

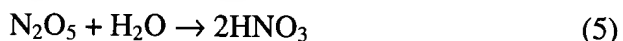
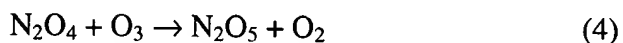
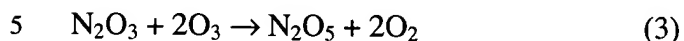
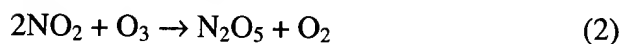
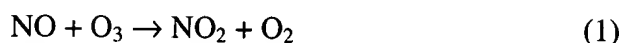
#### O<sub>3</sub> generating part

15 A common O<sub>3</sub> generator can be used directly. For example, pure oxygen gas (purity 99.99% or higher) from oxygen tank 10 first passed through flow rate regulator 11 and flow meter 12 and is then sent through pipeline 13 to O<sub>3</sub> generator 14, where O<sub>3</sub> is generated. The O<sub>3</sub>-containing oxygen gas is supplied to oxidation reaction chamber 16 through pipeline 15. It should be noted that NO<sub>x</sub> may also be formed in O<sub>3</sub> generator 14. Therefore, high-purity oxygen must be used for O<sub>3</sub> generator 14 or the O<sub>3</sub>-containing oxygen gas formed must be washed with an alkaline  
20 aqueous solution to remove the NO<sub>x</sub> through absorption and then dried through a drying agent, such as silica gel, etc.

#### Oxidation reaction part

25 In oxidation reaction chamber 16, the sample gas from pipeline 9 and the O<sub>3</sub>-containing oxygen gas from pipeline 15 are mixed and the NO<sub>x</sub> present in the sample gas is oxidized by O<sub>3</sub>.

The oxidation process can be represented by following equations (1) – (5).



Among these equations, equations (1) – (4) represent the oxidation reactions of  $\text{NO}_x$  with  $\text{O}_3$ .

10 Except for the reaction represented by equation (1), all other reactions result in the formation of  $\text{N}_2\text{O}_5$ . However,  $\text{N}_2\text{O}_5$  may further decompose to form  $\text{HNO}_3$  in the presence of water as shown in equation (5).

15 In order to prevent the problems caused by condensation of water from the sample gas, oxidation reaction chamber 16 should be maintained at a temperature higher than the boiling point of water, preferably at a temperature of  $110 \pm 5^\circ\text{C}$  using heating device 23, which consists of a heater and insulating material.

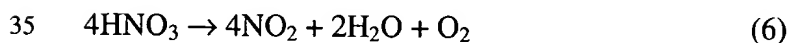
20 By using the temperature setting, the  $\text{NO}_x$  present in exhaust gas is completely converted to  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ , and  $\text{NO}_2$  through the oxidation process described above.

The amount of the  $\text{O}_3$  supplied to oxidation reaction chamber 16 should be in the range of 2 - 5 eq of the amount of the  $\text{NO}_x$  present in the exhaust gas. The capacity of oxidation reaction chamber 16 should be designed to achieve a retention time of the gaseous mixture in the range of  
25 5 – 20 seconds for sufficient reaction. The reaction chamber can be made of stainless steel, titanium, quartz, and glass.

#### Pyrolysis part

30 The sample gas, which is obtained from oxidation reaction chamber 16 and contains excess  $\text{O}_3$  and oxygen, is introduced through pipeline 17 to pyrolysis reactor 18.

In pyrolysis reactor 18,  $\text{HNO}_3$  and  $\text{N}_2\text{O}_5$  are decomposed to  $\text{NO}_2$  through the reactions represented by equations (6) and (8) {it should be (7). – Translator}







The excess  $\text{O}_3$  is also decomposed to  $\text{O}_2$  due to heat or the presence of  $\text{H}_2\text{O}$  and  $\text{NO}_2$ .

- 5 In order to achieve a smooth and rapid reaction, the reaction temperature should be higher than the boiling point of nitric acid, preferably about 180 - 650°C, maintained by using heating device 24, which consists of a heater and insulating material.

10 The capacity of pyrolysis reactor 18 and the materials used for the reactor can be the same as those for oxidation reaction chamber 16. However, in order to achieve a high reaction efficiency, a high specific surface area should be used. More specifically, a material with a high specific surface area, such as silica gel, alumina, etc., should be used to fill the reactor.

#### Measurement part

- 15 The  $\text{NO}_2$ -containing sample gas is then sent to gas-sealed sample cell 20 from pyrolysis reactor 18 through pipeline 19.

20 Gas-sealed sample cell 20 is equipped in the longitudinal direction with a combination of light source 26 and photoelectric tube 27, which is used to determine the concentration of  $\text{NO}_2$  using the strong UV absorption band of  $\text{NO}_2$ . Light source 26 can be, for example, a high-pressure mercury lamp, a tungsten lamp, or a xenon lamp. The signal received by photoelectric tube 27 is sent through amplifier 28 to recorder 29.

25 Gas-sealed sample cell 20 has a length of 10 m {sic!} for the optical pass. By using a light source with a wavelength of 596 nm, the concentration of the  $\text{NO}_2$  present in exhaust gas was determined. Figure 2 shows the relationship between the transmittance ( $I/I_0$ ) and the concentration. Moreover, the detection limit and measurement accuracy obtained from the experiment are shown in Table 2.

30 Table 2

	Single-beam detection mode	Double-beam detection mode
Lower detection limit	8 ppm	1 ppm
Reading error	$\pm 1$ ppm	$\pm 0.1$ ppm

After the concentration of  $\text{NO}_x$  is determined, the sample gas is then released from the system through pipeline 21.

In order to prevent the problems caused by condensation of water from the sample gas, the measurement part, consisting of pipeline 19, gas-sealed sample cell 20, and pipeline 21, is maintained at a temperature higher than the boiling point of water, preferably a temperature of 101[?] - 110°C, using heating device 25, which consists of a heater and insulating material.

Next, another practical example of this invention is explained using Figure 8. This is a practical example using ESR for the detection, so that the quantitative determination of NO<sub>2</sub> is not affected by the H<sub>2</sub>O presence in the sample gas.

In the practical example, the procedures for exhaust gas sampling, oxidation with O<sub>3</sub>, and pyrolysis of NO<sub>x</sub> to NO<sub>2</sub> are the same as in the practical example shown in Figure 1. Then, the NO<sub>2</sub>-containing sample gas, maintained at a temperature higher than the boiling point of water, is introduced into the detecting part of ESR 30. The concentration of NO<sub>x</sub> is determined by utilizing the Zeeman effect of NO<sub>2</sub>.

As shown in Figure 4, when NO<sub>2</sub> is further converted to NO, the concentration of NO<sub>x</sub> can be determined by using CLA as a detector for NO.

In the figure, the NO<sub>2</sub>-containing sample gas coming from pyrolysis reactor 18 is introduced through pipeline 19 to NO<sub>2</sub>-converter 31, where NO<sub>2</sub> is further reduced to NO. The procedures used before pyrolysis reactor 18 are the same as those used in the previous practical example. The NO-containing sample gas coming from NO<sub>2</sub>-converter 31 is sent through pipeline 32 to dehydration device 33 using an electronic cooling system to remove the water, which is harmful to the subsequent CLA detector, and then to CLA 34. The concentration of NO<sub>x</sub> present in exhaust gas is determined by measuring the concentration of NO in the sample gas.

In this practical example, NO<sub>2</sub>-converter 31 can be, for example, a commonly used converter using a M<sub>o</sub>-based catalyst operating at a temperature of 350 – 450°C or a stainless steel system {sic!} operating a temperature of 600°C. These systems are sensitive to moisture and may have insufficient reduction for HNO<sub>3</sub>. However, the methods for the analysis of nitrogen oxide using these systems are covered by the scope of this invention,

Moreover, NO<sub>2</sub> is converted to NO in NO<sub>2</sub>-converter 31. Since NO has very low reactivity towards water, the loss of NO at dehydration device 33 is about 0.8% or lower of the total amount of NO<sub>x</sub> present in exhaust gas.

#### 4. Brief description of the drawings

Figure 1 is a flow chart showing a practical example of this invention. Figure 2 shows the results obtained from the determination of NO<sub>x</sub> present in an engine exhaust gas using the system

5 described in Figure 1. Figure 3 and Figure 4 are flow charts showing the NO<sub>x</sub> measurement parts of two different practical examples of this invention, respectively.

	1	Exhaust gas source	3	Dust filter
	5	Pump	14	O <sub>3</sub> generator
10	16	Oxidation reaction chamber	18	Pyrolysis reactor
	20	Gas-sealed sample cell		
	22, 24	Heating devices		
	26	Light source		
	27	Photoelectric tube		
15	30	ESR		

Agent: Takehiko Suzue, patent agent

Figure 1

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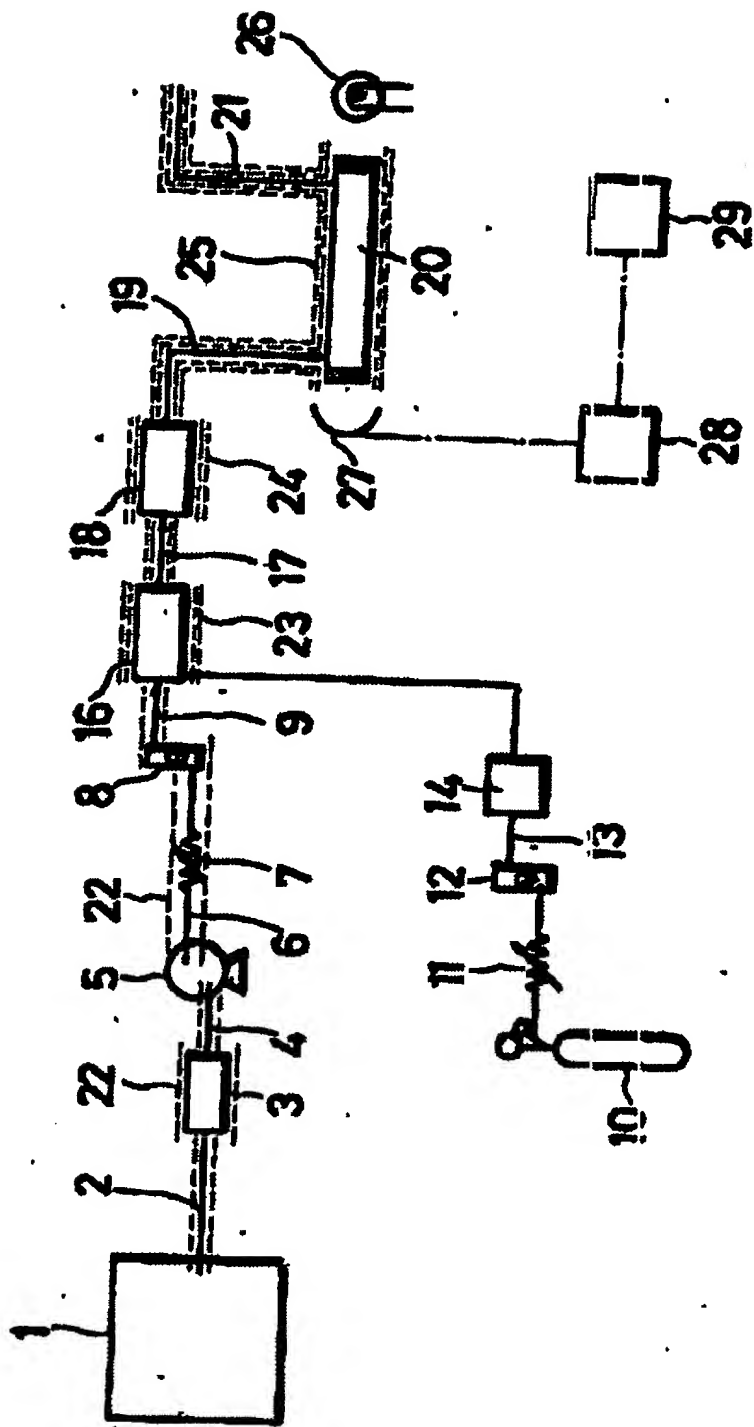


Figure 2

ordinate: Transmittance ( $I/I_0$ )

abscissa:  $\text{NO}_2$  concentration (ppm)

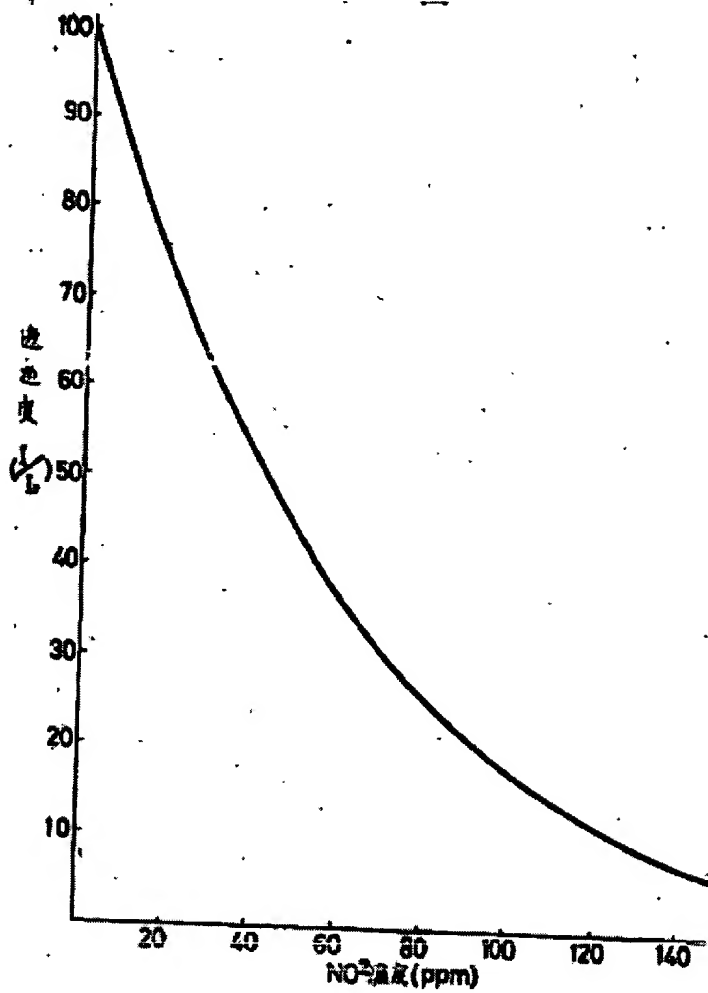


Figure 3

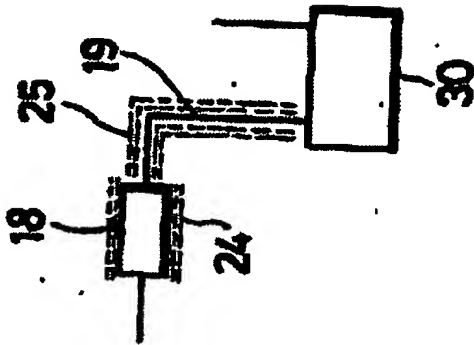
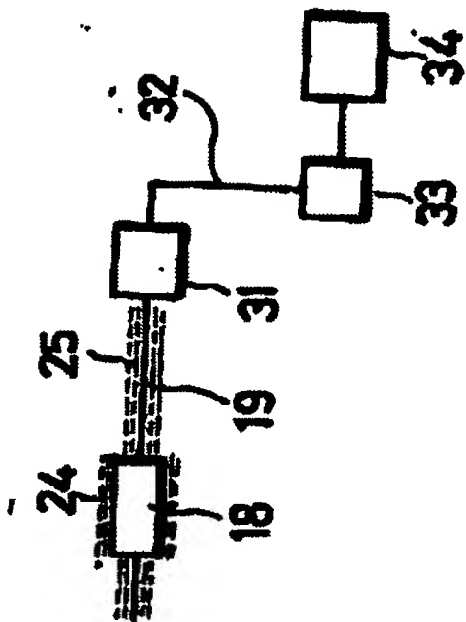


Figure 4



5 Amendment

All corrections have been incorporated into the English version. -- Translator